

LOW DETONATION PRESSURE EXPLOSIVES

M. T. Abegg *

H. J. Fisher **

H. C. Lawton **

W. T. Weatherill **

* Sandia Corporation, Albuquerque, New Mexico

** Aerojet-General Corporation, Downey, California

Most explosive materials in wide use today may be characterized by detonation pressures ranging from approximately 150 to 350 kilobars. Propellant materials, on the other hand, exhibit comparatively low pressures typical of deflagration reactions. The difference in pressures exhibited by these two classes of materials leaves an interesting gap, the exploration of which may yield valuable information on the chemical and kinetic limitations of detonating materials.

The reliable generation of detonation pressures under 100 kilobars should offer advantages from an engineering standpoint in applications where higher pressures are neither needed nor desired. Certain plastic/explosive formulations described below offer these advantages in addition to others, such as the capability of being extruded or injection molded into difficult configurations and then polymerized in place.

Over the past two years the Aerojet-General Corporation and the Sandia Corporation have collaborated in a preliminary investigation of this interesting low detonation pressure regime. The results recorded below describe some of the courses pursued and techniques developed in this study to date.

EXPERIMENTAL TECHNIQUES

a. Material Specifications

All chemical ingredients utilized in the formulation of the plastic-explosive compositions described herein were purchased to meet pertinent military specifications. Because of the importance of the particle size distribution of the primary and secondary explosives used, tests were run to measure this by microscopic techniques using a Filar eyepiece. The particle size distributions of pentaerythritol tetranitrate (PETN), superfine grade; cyclotrimethylenetrinitramine (RDX), acetone fine; eight hour ball-milled dextrinated lead azide (PbN_6); coarse dextrinated PbN_6 ; and thallous azide (TlN_3) are presented in Figs. 1 through 4, respectively.

b. Formulating Techniques

Of primary consideration in working with new explosive formulations are the compatibility of the various ingredients and general safety precautions. Initially, in all cases, small quantities (about 1/10 gram) were used, and if no adverse reaction resulted the quantities were increased to one gram, 10 gram, and 100 gram lots. Analyses were made to determine the compatibility and stability of the compositions at the 10-gram level. Among the tests used were vacuum stability, impact sensitivity, differential thermal analysis (DTA), and, in some cases, explosion temperatures. The results of such tests are shown in Table 1.

Safety precautions common to the explosive industry were rigorously observed along with many laboratory precautions used in the chemical industry. In all cases while working with small quantities of materials (under 10 grams) work was conducted behind adequate safety shields. When working with larger quantities, the mixing procedures were carried out with remote control methods, viewing the processes through mirrors, periscopes or closed circuit television. Explosives were handled and stored in conducting rubber containers. The quantity of explosive materials was limited to 50 grams in the laboratory. In the mixing buildings, the materials were limited to the actual quantities needed.

c. Rheological Characteristics

During the formulation of high-solids-content compositions extremely viscous, putty-like systems were encountered. It was found that the addition of small quantities (0.1 to 1.0 percent) of special surfactants caused a significant increase in the fluidity.

Changes in the rheological characteristics were determined by the use of a parallel plate plastometer technique. A small cylindrical sample of the paste-like test sample was placed upon a glass plate and loaded with another glass plate of known weight. The radius to which the sample spread after 30 seconds' duration was taken as an indication of the apparent fluidity of the test system. The greater the radius, the greater the effectiveness of the surfactant.

d. Testing Procedures

Detonation Velocity Measurements - Detonation velocity measurements were carried out using two well-known methods, the streak camera and pin switch techniques. A Beckman-Whitley Model 194 streak camera was utilized. Ionization pin switches in conjunction with a mixer circuit and Moran Model 101A raster oscilloscope were also used to measure detonation velocities of both confined and unconfined charges. The ionization pin switches were mounted in special holding devices and distances were measured with a Gaertner Scientific Corporation microcomparator capable of measurement to ± 0.002 millimeters. All velocity measurements were started at least four diameters from the point of initiation.

Detonation Pressure Measurements - The detonation pressure measurements were carried out using a modified plate dent test. Attempts were also made to use the aquarium technique.

The modified plate dent test consisted of 20 grams of explosive material in a copper tube (3/4 in. x 5 in. x 1/16 in. wall). The detonation was initiated by an Engineer's Special blasting cap with a five-gram booster of Composition C-4. An aluminum witness plate (1 3/4 in. x 5 in. x 5 in. of 6061-T6 alloy) was used. This technique was used to determine the approximate detonation pressure range of the various formulations.

A series of calibration tests using standard explosives of varying densities was conducted to determine detonation pressure as a function of depth of indentation in the witness

plates. Detonation velocities as a function of density for each explosive were obtained from W. R. Tomlinson⁽¹⁾ and O. E. Sheffield⁽²⁾. Detonation pressures were calculated from the detonation velocities at known densities of the explosives by the approximate equation⁽³⁾

$$p \approx 0.010 \rho \frac{D^2}{4}$$

where:

(1)

p = detonation pressure in bars

ρ = density in grams per cubic centimeter

D = detonation velocity in meters per second

A review of other possible methods of measuring detonation pressures of large samples (2 in. diameter x 8 in. length) indicated that the "aquarium" technique originally developed by Holton⁽⁴⁾ and later described by Cook, Keyes and Ursebach⁽⁵⁾ appeared to offer good possibilities for application in this test program. In this method a streak camera is used to measure the detonation velocity of the plastic explosive and also the velocity of the resultant shock wave through water. From the measured velocity of the shock wave together with the equation of state of water, it is possible to calculate the shock pressure in water. However, a considerable number of problems were encountered in attempts to measure pressures by this technique. The principal objection lay in the ambiguity of the slope of the shock at the explosive/water interface. This ambiguity seemed to be more pronounced at lower shock pressures. Accordingly, this technique was abandoned and all of the pressure data reported here are based on plate dent and $1/4 \rho D^2$ approximations.

e. Sensitivity Tests - Sensitivities and compatibilities of the various explosive formulations were determined by impact, vacuum stability and differential thermal analysis. These methods are discussed in Ref. 2. The impact tests were run on a modified Bureau of Mines machine using a two-kilogram weight and flat anvil and striker. It was found that nitronolyurethane (NPU)/PETN and NPU/RDX formulations, containing concentrations of 20 percent by weight of explosive or larger quantities, were can sensitive to Number 8 blasting caps. Compositions containing smaller quantities of these explosives required the use of a booster to insure initiation. However, in most of the firing tests a five-gram booster charge of Composition C-4 together with an Engineer's Special detonator were employed to insure initiation.

EXPERIMENTAL RESULTS

a. Compositions - The compositions of the plastic explosive formulations studied consisted of polyurethane, nitropolyurethane, and dinitropronyl acrylate matrices (continuous phase) to which various explosives (discrete phase) were added. The polyurethanes were composed of diols/triols or other cross-linking agents/diisocyanate, in 70/30/107 mole percents, together with 20 percent plasticizer. The nitronolyurethanes were composed of diols/triols or other crosslinkers/nitrodiisocyanate together with up to 50 percent by weight of nitro plasticizer. In the NPU formulation, the diol/triol/isocyanate ratio was 80/20/107 mole percents.

b. Chemical and Physical Properties - The chemical and physical properties were determined for each of the compositions and are given in Table I. The vacuum stabilities and DTA's were determined to ascertain the stability of several compositions to thermal decomposition. The vacuum stability data showed that in all cases the mixtures had satisfactory stability.

The DTA's for NPU and NPU/PETN formulations are given in Figs. 5, 6 and 7 and similar information for PU/PbN₆ mixtures is given in Figs. 8, 9 and 10. The data indicate that

the final compositions in both cases are as thermally stable as that of the least stable component. The compatibility of the individual ingredients and combinations thereof was determined for each of the formulations. It was found that both PETN and RDX are compatible with the ingredients of the PU and NPU plastic formulations. Similar studies using NPU and PU systems with lead and other azides showed that the nitro substituted plasticizing agents and nitro substituted diisocyanates were incompatible with azides; however, it was found that the components of the PU system were compatible with the azides.

The densities of the various formulations varied from that of the pure plastic binder system up to that of the pure discrete phase. In the case of the NPU/PETN systems, the densities were found to vary from 1.2 g/cm³ up to about 1.35 g/cm³ depending upon the concentration of the discrete phase. In the plastic/PbN₆ systems, the densities varied between that of the binder system up to 2.1 g/cm³ depending upon the concentration of PbN₆.

In high-solids-content plastic explosive compositions, the rheological characteristics are important. In one system composed of 30 percent DNPA (dinitrononylacrylate) binder system and 70 percent RDX, it was found necessary to add 10 percent calcium stearate, impalpable grade, by weight to prevent dilatancy while extruding the plastic composition under pressure. The large amount of calcium stearate (CS) acts as a phlegmatizing agent making it more difficult to propagate a detonation. It was advisable to find methods for reducing the required amount of CS and at the same time to increase the fluidity of the plastic/explosive mixture.

Earlier studies with propellant formulations had shown that pretreatment with small amounts of surface active agents caused a large increase in fluidity. In preliminary studies with RDX and PETN, the desired amount of surface agent was dissolved in methyl alcohol or chloroform and the explosive treated with the solution. The solvent was evaporated and the explosive was dried in vacuo, leaving a film of surfactant on the surface of the explosive.

Tests showed that SPAN 60 (Atlas Chemical Company) and calcium stearate, impalpable grade, were the most effective fluidizing agents tested. Using the above pretreatment technique, the maximum increase in fluidity occurred when using calcium stearate at a concentration of 0.5 percent by weight, and the fluidity decreased with further increase in concentration. Similarly, the maximum advantage of SPAN 60 alone was found to be at 0.25 percent by weight. In some systems a synergistic effect was observed with calcium stearate and SPAN 60 at similar concentrations. The DNPA/RDX mixtures showed a marked increase in fluidity after standing for three hours. Similar results were obtained with other highly loaded plastic explosive systems.

The reduction in the amount of calcium stearate in the explosive composition from 10 percent to 0.5 percent resulted in increased fluidity and ease of extrusion together with a significant increase in detonation velocity.

c. Explosive Properties - Tests were conducted to determine the effect of solids concentration, confinement and diameter on the explosive characteristics (detonation velocity and pressure) of the plastic explosive compositions. The compositions, diameter and confinement of samples tested are shown in Table II. Detonation velocity measurements were carried out on at least five charges for each diameter except with 3.58-inch diameter charges, where only three were tested. The effects of explosive concentration and charge diameter on detonation velocity are shown in Figs. 11 and 12. The data in Fig. 11 show that the detonation velocity increases in the usual fashion with an increase in diameter. It is of interest to note that 1/16 inch copper confinement had no apparent effect on detonation velocities in the charge diameter range from 1.0 inch to 1.875 inch. The 20 percent PETN - 80 percent NPU formulation reaches ideal detonation velocity at a diameter of 3.4 inches, compared with 3 inches for the 25 percent PETN - 75 percent NPU formulation. The data in Fig. 12 show that the detonation velocity

increases as expected with increase in explosive content. The data in Table III show the approximate minimum diameters at which detonation is sustained for the various compositions either unconfined or confined in 1/16-inch wall copper tubing.

d. Detonation Pressure - In preliminary experiments the calibrated plate dent method for determining detonation pressure was used to estimate the approximate detonation pressure for the various compositions. In those experiments where detonation velocities were determined, it was considered adequate for present purposes to calculate the approximate detonation pressure from the $1/4 \rho D^2$ relationship. Detonation pressures calculated in this fashion are shown as a function of explosive composition in Fig. 13. These data show that the detonation pressures range from 25 to approximately 160 kilobars for the compositions tested.

Preliminary studies with PU/PbN₆ systems indicated that a system containing 40 percent PU/60 percent PbN₆ by weight will just sustain detonation. Plate dent tests indicated that the detonation pressure would be under 10 kilobars. A 30 percent PU/70 percent PbN₆ composition had a detonation pressure of approximately 22 kilobars as determined by the plate dent test. A typical witness plate from a plate dent test is shown in Fig. 14. It thus appears that detonation pressures in the very low pressure range may be obtained with PU/PbN₆ systems.

e. Impact Sensitivity - Impact sensitivities for the various explosives were measured as shown in Table I. It was found that the addition of secondary and sensitive primary explosives to the PU or NPU binder systems resulted in compositions much less sensitive to impact.

DISCUSSION OF RESULTS

The formulation of explosives composed of a high-energy discrete phase in a continuous matrix of combustible organic material necessarily involves an excursion into a number of physical and chemical problems. In general, this investigation was built around the incorporation of relatively sensitive explosives into a plastic such that inter-particle distances were relatively large. The composition of the plastic explosives ranged from 10 to 70 percent discrete phase by weight with corresponding amounts of poly and nitro polyurethanes, and other plastics.

The physical and chemical properties of this type of explosive imply a versatility not normally encountered with explosive materials. Prior to polymerization, the compositions are extrudable under pressure and readily assume the shape of the container. They bond readily to clean metal surfaces. They are capable of being introduced into irregularly shaped volumes and polymerized in place. Once the materials are polymerized they exhibit properties related to those of the plastics involved.

An interesting effect of average particle size on the ability of certain formulations to be initiated was observed. When the concentration of PbN₆ in polyurethane was held at 60 weight percent, initiation was not achieved at an average particle size of one micron, but was achieved at average particle sizes ranging from five to ten microns, using the same initiating charge. The region above this range has not yet been explored.

A marked effect on the extrudability of the non-polymerized compositions was achieved by the use of surfactants at concentrations of the order of 1/10 to one percent. The effect of surface active materials on the rheological characteristics of explosive compositions was pronounced and served to extend the useful range of these materials.

The incorporation of sensitive primary explosives into an inert plastic matrix introduces another family of explosive compositions. Their ability to inter-initiate from particle to particle through the continuous phase of the composition opens up other areas of low pressure explosive technology.

ACKNOWLEDGMENTS

This work was performed under the auspices of the United States Atomic Energy Commission. The cooperation of the Bureau of Explosives in the classification of new formulations is gratefully acknowledged. The technical assistance of Messrs. R. F. Van Cleave and B. R. Wenfer in the formulation of the explosive compositions, and Mrs. J. T. Knight in data reduction and preparation of the manuscript is greatly appreciated.

- (1) W. R. Tomlinson, Jr., Properties of Explosives of Military Interest, Picatinny Arsenal, Technical Report No. 1740, 20 June 1949.
- (2) W. R. Tomlinson, Jr., revised by O. E. Sheffield, Properties of Explosives of Military Interest, Picatinny Arsenal, Technical Report No. 1740, Revision No. 1, April, 1958.
- (3) M. A. Cook, The Science of High Explosives, Reinhold Publishing Corporation, New York, 1958, p. 35.
- (4) W. C. Holton, The Detonation Pressures in Explosives as Measured by Transmitted Shocks in Water, NAVORD Report 3968, 1 December 1954.
- (5) M. A. Cook, R. T. Keyes and W. O. Ursenbach, Measurements of Detonation, Shock and Impact Pressures, Third Symposium on Detonation, ONR ACR-52, Vol. 2, p. 357, ASTIA No. 242 585.

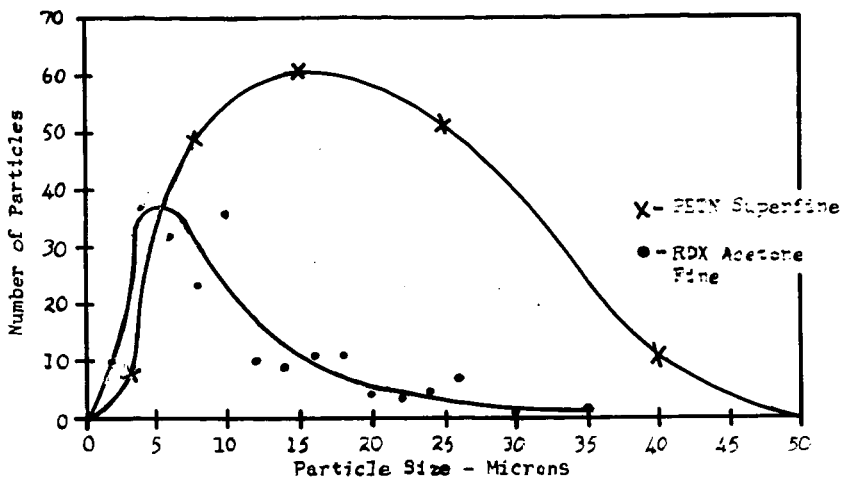


Fig. 1.—Particle Size Distribution of RDX and PETN
(200 particles counted)

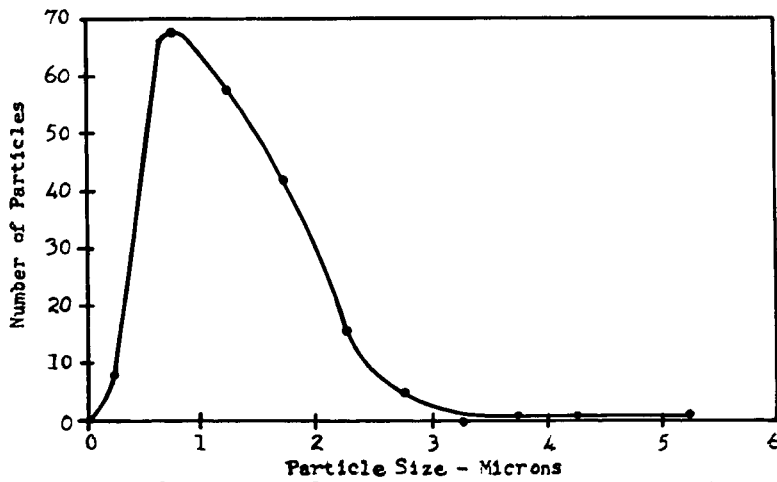


Fig. 2.—Particle Size Distribution of Milled Dextrated PBX₅
(200 particles measured)

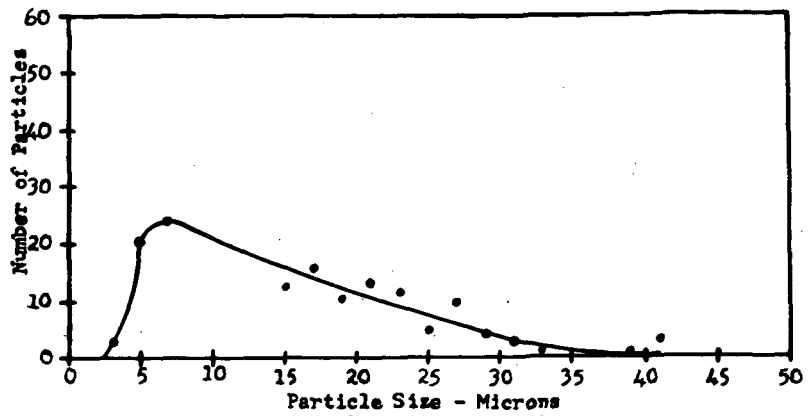


Fig. 3.—Particle Size Distribution of Coarse PbN_6
(200 particles measured)

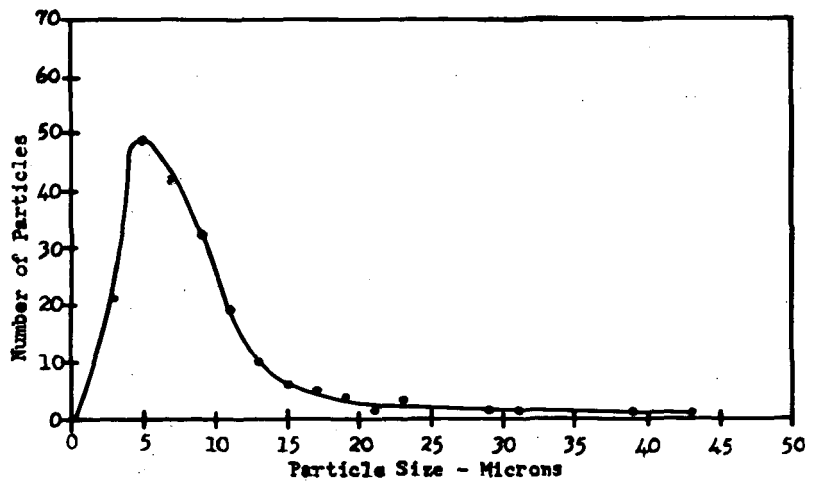


Fig. 4.—Particle Size Distribution of TLN_3
(200 particles counted)

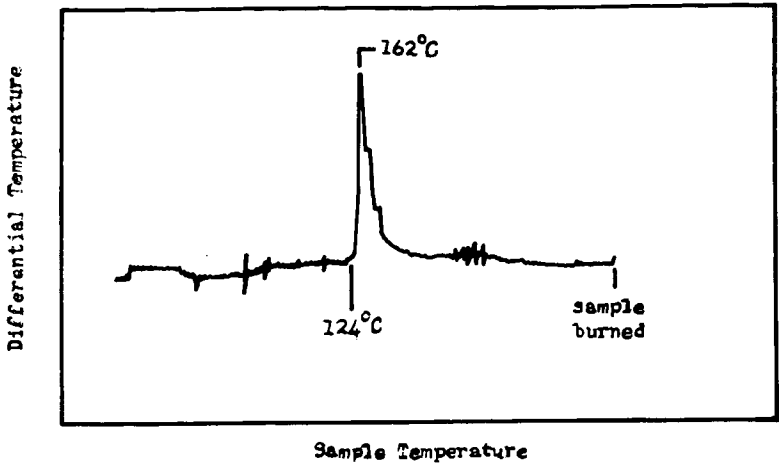


Fig. 5.—DTA - NPU

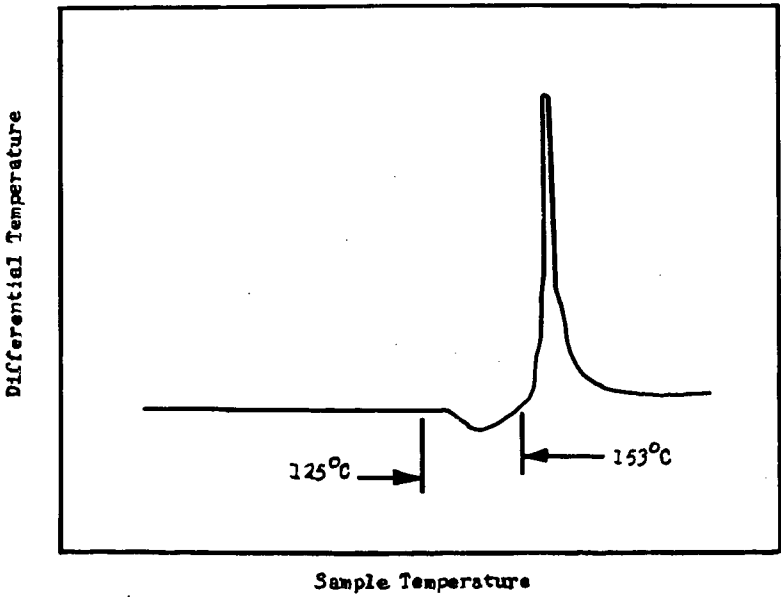


Fig. 6.—DTA - PETN

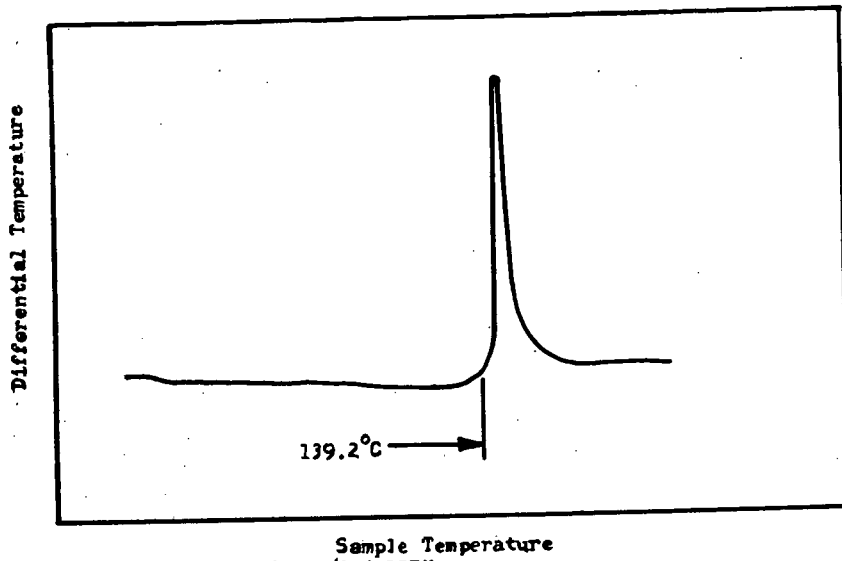


Fig. 7.—DTA - 70% NPU/30% PETN

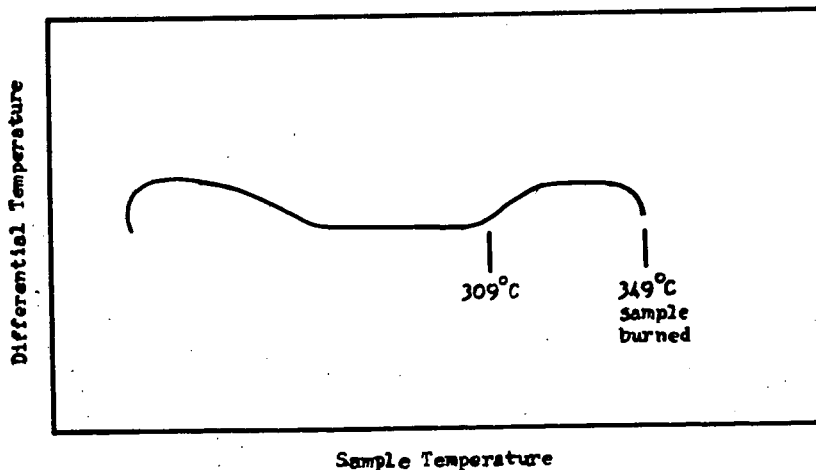
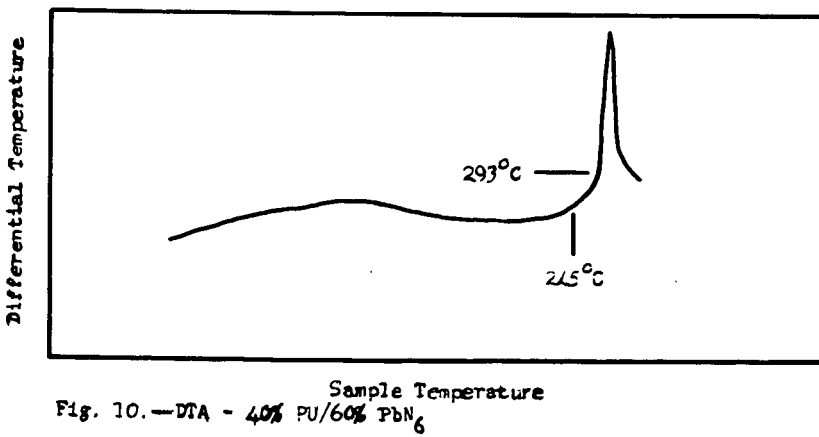
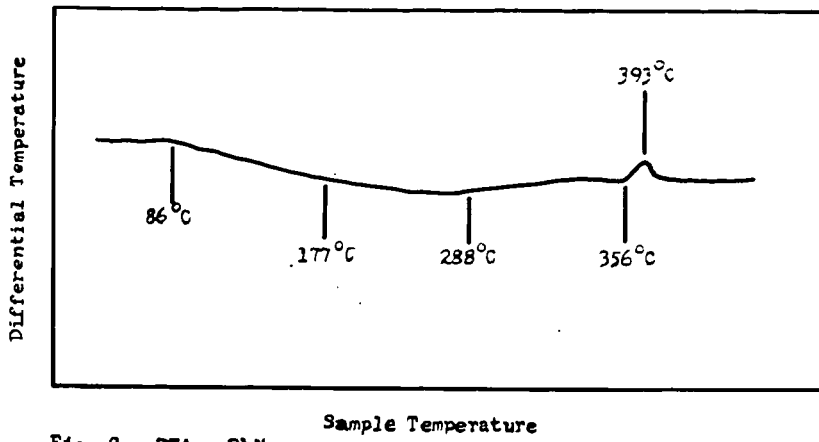


Fig. 8.—DTA - PU



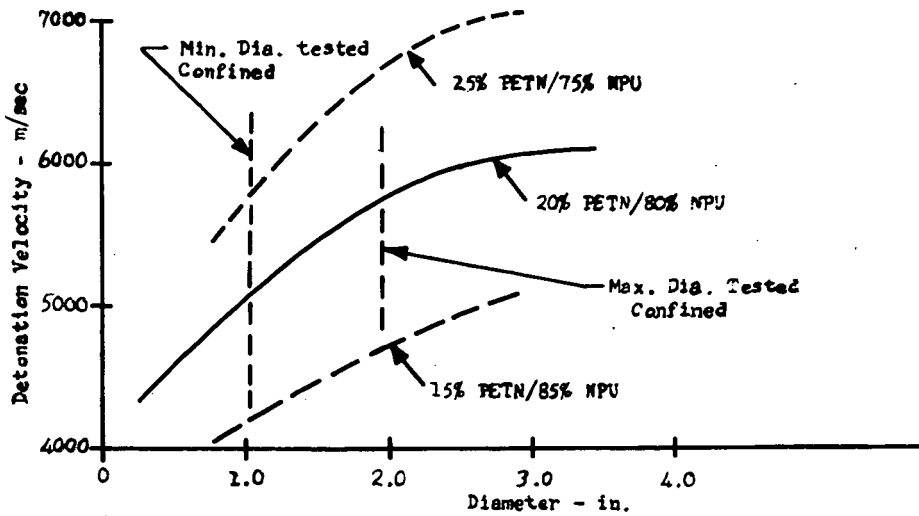


Fig. 11.—Effect of Dia. on the Detonation Velocity

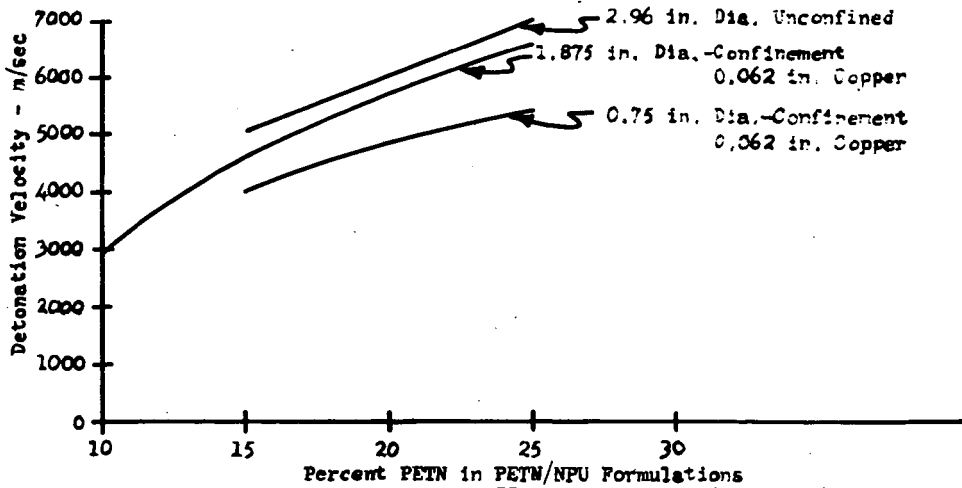


Fig. 12.—Effect of the Percent PETN on the Detonation Velocity

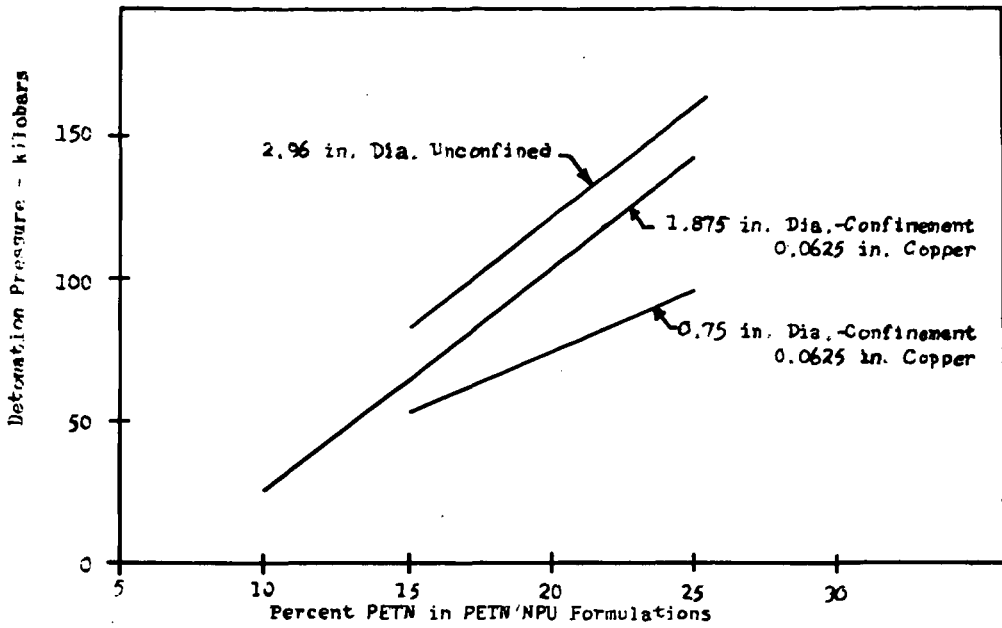


Fig. 13. —Effect of the Percent PETN on the Detonation Pressure

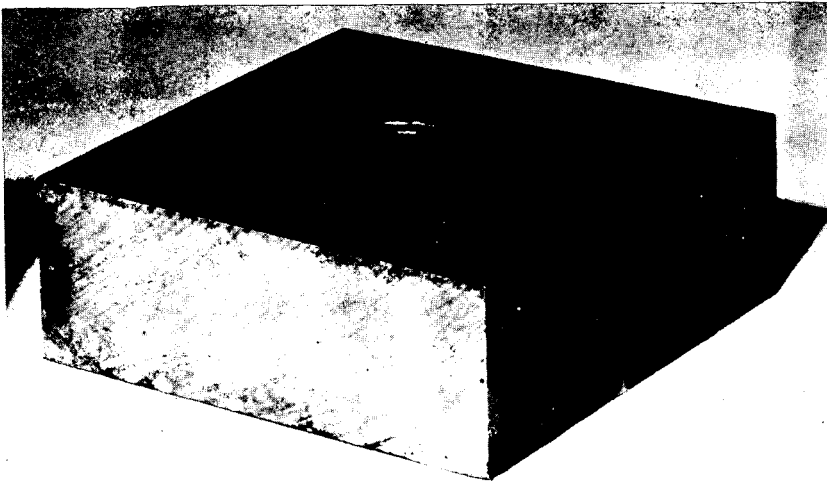


Fig. 14.—Test No. 194

Chg. Dia. $3/4$ in.	Confinement $1/16$ in. thick Aluminum
Chg. Lgth. $4-3/8$ in.	Witness Plate 5 in. X 5 in. X $1-3/4$ in.
Chg. Density 2.06 g/cc	6061-T6 Aluminum
Depth of Dent .145 in.	Approx. Detonation Pressure - 22 Kb

TABLE I
PHYSICAL AND CHEMICAL CHARACTERISTICS
OF PLASTIC EXPLOSIVE FORMULATIONS

Property	30% PETN 70% NPU	30% RDX 70% NPU	60% PBN ₆ 40% PU	60% TIN ₃ 40% PU	PBN ₆ TIN ₃ milled	RDX	PETN	NPU
Density at 25°C (g/cc)	1.345	1.385	-	-	4.38	3.68	1.82	1.77 1.21
Vacuum Stability at 100°C (cc's of gas/g/4.0 hr)	* 0.015	* 0.064	0.60	0.16	0.1	-	0.7	0.5 0.32
DTA Exotherm at °C	139.2	161.5	293	317	356	-	161.5	139.2 124
Impact Sensitivity (cm/2kg)								
100%	60	65	100	140	1	3	27	14 >200
50%	51	58	82	172	1	1/2	22	11 >200
0%	43	50	70	190	1	1/2	19	8 >200

* Vacuum stability at 180°F

TABLE II
TEST SAMPLES FOR DETONATION VELOCITY

Composition (%)		Charge Diameter (in.)											
		Confined*							Unconfined				
		0.25	0.50	0.75	1.125	1.375	1.875	1.0	1.45	1.81	2.56	2.96	3.58
PETN	NPU												
10	90			X			X					X	
15	85			X			X					X	
20	80	X	X	X	X	X	X	X	X	X	X	X	X
25	75			X			X					X	

* Confinement in all cases was copper tubing with 1/16-in. wall thickness

TABLE III
 APPROXIMATE CRITICAL DIAMETERS OF SEVERAL
 NPU-PETN FORMULATIONS

FORMULATION (% PETN/% NPU)	CONFINEMENT	CRITICAL DIAMETER (in.)
10/90	CONFINED*	1.87
10/90	NONE	Greater than 2.96
15/85	CONFINED*	0.5
15/35	NONE	Greater than 1.0
20/80	CONFINED*	0.25
20/80	NONE	
25/75	CONFINED*	Less than 0.25
25/75	NONE	Less than 1.0

* All confined charges were confined in
 1/16 in. wall copper tubing.